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Abstract

A critical problem area in semiconductor electrochemistry is that of non-radiative transition rates at the semiconductor-electrolyte interface a subject of intense investigation in recent times As surface modifications such as chemisorption seem to have a significant effect on interfacial kinetics, chemisorbate induced localized levels are seen to act either as surface recombination centers and/or mediate charge transfer across the interface Thus, clarifying the role of these interfacial states as well as characterizing them is an important step in understanding phenomena at the interface

Specifically by employing a kinetic model for the steady-state surface recombination we obtain an almost linear relation between the energy of a discrete surface level in the band gap and either the potential at which recombination flux reaches a maximum or the potential at which faradaic flux undergoes an inflexion These results are unique to the semiconductor electrolyte context since they involve faradaic processes unlike in semiconductor surface physics As the next step, we model transient photocurrents as arising from surface-state relaxation Assuming a kinetic form for surface minority carrier relaxation we couple the above two processes and study their mutual evolution via a master equation and the effect of such a coupling on photocurrent transients The analysis of both steady-state and transient results show that the energy of the surface state is in principle determinable from transient measurements

The time behaviour of minority carriers under conditions of depletion and low illumination is a problem of great theoretical and experimental importance Analytical expressions are obtained to describe surface minority carrier relaxation under steady-state illumination This is shown to be critically dependent on depletion layer potential as it is possible to shift from an integral equation description to a kinetic form by potential variations Thus, questions concerning the validity of kinetic forms for minority carrier relaxation and its time scales of relaxation in the context of its possible coupling/decoupling to surface state relaxation are addressed

After deriving the general solution to the continuity equation for the minority carriers, we use this to derive generalised expressions for the output signal pertinent to time resolved microwave and luminescent experiments under depletion condition Apart from the pulse form other forms of illumination such as switch on and off transients periodic and steady state modes as well as their various interrelationships are considered The importance of a depletion layer as an additional experimental variable is seen in its being able to effect pure exponential forms of carrier relaxation as well as determine the dominant channel for carrier relaxation at the interface

The scope of the model outlined above is further enlarged by incorporating two independent features observed in carrier relaxation experiments viz (i) self absorption associated with the emitted luminescence signal and (ii) focussing or the effect of a finite numerical aperture both of which introduce new time scales in the problem of carrier relaxation The inter play between the electric field and the parameters which characterize these effects and the consequent modulation of the intensity and time scales of carrier decay signals are analysed

Since the origin of the surface level and the trapping process therein are both quantum mechanical in their description we obtain expressions for the microscopic anodic current that is mediated by interfacial states A transfer Hamiltonian formalism is used to represent the various system components and the expression for current is evaluated via the theory of linear response The density of states of the interfacial level analysed for various mechanisms of transfer, is seen to be rich in structure (owing to a phonon subsystem whose coupling strength is included to all orders) and are pertinent to STM measurements made in the electrochemical tunneling mode